

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup>:</b> <b>C09D 7/12, C09C 1/30 // C09D 163/00</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 98/58030</b> <b>(43) International Publication Date:</b> 23 December 1998 (23.12.98)
<b>(21) International Application Number:</b> PCT/GB98/01588 <b>(22) International Filing Date:</b> 1 June 1998 (01.06.98) <b>(30) Priority Data:</b> 9712591.8 16 June 1997 (16.06.97) GB <b>(71) Applicant (for all designated States except US):</b> CROSFIELD LIMITED [GB/GB]; Bank Quay, Warrington, Cheshire WA5 1AB (GB). <b>(72) Inventor; and</b> <b>(75) Inventor/Applicant (for US only):</b> MOREA-SWIFT, Gemma [IT/GB]; 8 Branden Drive, Knutsford WA16 8EJ (GB). <b>(74) Agents:</b> COLLINGWOOD, Anthony, Robert et al.; ICI Group Intellectual Property, The Heath, P.O. Box 11, Runcorn, Cheshire WA7 4QE (GB).	<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>	
<b>(54) Title:</b> MATTING PASTE FOR CATIONIC SYSTEMS  <b>(57) Abstract</b>  The use of 10-40 wt.% of diluents such as vinyl ethers (such as CHVE, DVE3) and acrylates (HDDA, TPGDA, DPGDA) alongside the cycloaliphatic epoxy greatly enhances the porous silica effect and allows to manufacture matt and semigloss coatings based on cationic or hybrid (cationic/free radical cure) without detriment of other desired film properties.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakhstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

Matting Paste for Cationic SystemsTechnical field of the Invention

5

The present invention relates to a matting paste for cationic systems.

Background of the Invention

10

The use of synthetic porous silica to obtain a matt finish in paints, varnishes and lacquers is known. It is particularly known to use silica in solvent and water based coatings. The effect of gloss reduction by silica is commonly associated with the solvent evaporation and film volume decrease which takes place during the drying of the coating.

15

20

100% solid coatings formulations can be manufactured which will crosslink under Ultra Violet light. They contain oligomers, photoreactive initiators and various additives.

25

30

With the increasing popularity of radiation cured coatings in a wide variety of applications, the ability to control and reduce gloss is becoming more important. In 100% solid UV curable coatings large quantities (up to 15% wt.) of porous silicas or large particle size silicas are required to achieve a matt or semi-gloss finish, since curing in UV curable coatings is associated with minimum film shrinkage and no solvent evaporation. These approaches, are limited by the increase in viscosity of the varnishes when large concentrations are used, or the roughness of cured films, when large APS are used.

35

Three major classes of photocurable resins may be used in UV formulations: i) acrylated oligomers, ii) unsaturated polyesters and iii) cycloaliphatic and bisphenol A epoxies. Acrylated oligomers and unsaturated polyesters can  
5 polymerise and crosslink when they are mixed with chemicals which produce free radicals when exposed to Ultraviolet light. Cycloaliphatic and bisphenol A epoxies can polymerise and crosslink when they are mixed with sulphonium salts which decompose under Ultraviolet light, produce an acid  
10 catalyst which initiate the reaction. This mechanism of curing is defined "Cationic Curing".

The gloss of formulations containing acrylated oligomers and unsaturated polyesters can be successfully reduced using the  
15 above approaches.

In epoxy resin based formulations, which cure following the cationic mechanism, large particle size and even very large concentrations of silica do not cause a decrease of the  
20 gloss of the dry film. These formulations, although preferred in a number of applications, for their abrasion resistance, hardness and temperature resistance cannot be easily manufactured with a matt or semi-gloss finish.

25 There is therefore a need for a matting system which can be used in cationic curable systems.

It has now surprisingly be found that the use of 10-40% wt. of diluents such as vinyl ethers (such as CHVE, DVE3) and  
30 acrylates (HDDA, TPGDA, DPGDA) alongside the cycloaliphatic epoxy greatly enhances the porous silica effect and allows to manufacture matt and semi-gloss coatings based on cationic or hybrid (cationic/free radical cure) without detriment of other desired film properties.

Test Procedures and Definitions

## i. Nitrogen Surface Area-Pore Volume

Nitrogen surface area is determined by standard nitrogen adsorption methods of Brunauer, Emmett and Teller (BET) using a multipoint method with an ASAP 2400 apparatus supplied by Micromeritics of the USA. The samples are outgassed under vacuum at 270 deg.C for at least one hour before measurement. Surface area is calculated from the volume of nitrogen gas adsorbed at  $P/P_0$  0.98. This apparatus also provides the pore size distribution from which it is possible to get the pore size ( $D_{10}$ ) for which 10% of the pores are below this pore size. In the same manner is possible to get the pore size for which 50% ( $D_{50}$ ) and 90% ( $D_{90}$ ) of the pores are below this pore size. Additionally the pore volume (cm<sup>3</sup>/g) for a given range of pore size can be obtained from the desorption curve.

## ii. Weight mean particle size

The weight mean particle size is determined with the aid of a Malvern Mastersizer using a 100 mm path length lens. This instrument, made by Malvern Instruments, Worcestershire uses the principle of Fraunhofer diffraction utilising a low power He/Ne laser. Before measurement the sample is dispersed ultrasonically in water for a period of 7 minutes to form an aqueous suspension. The Malvern Mastersizer measures the weight particle size distribution of the silica. The weight mean particle size ( $d_{50}$ ), the 10 percentile ( $d_{10}$ ) and the 90 percentile ( $d_{90}$ ) are easily obtained from the data generated by the instrument.

## iii. Matting efficiency

In order to test the matting efficiency the following formulation has been prepared according to the following procedure.

## Formulation:

UVR6110 *	81.5 - X%
Vinyl ether	X
UVR6990 *	3.0%
Fluorad FC430 #	0.5%
Silica	15%
* ex. Union Carbide	
# ex. 3M	

The resin, diluent, additive and photoinitiator were weighed in an amber brown jar and stirred for 30 seconds at 500 rpm using an Heidolph stirrer equipped with Cowles head. The silica was then added and all was stirred at 3000 rpm for ten minutes. The system was allowed to deaerate and then drawn down onto black Leneta 7C cards using a 25 microns K-Bar applicator. The cards were cured at 3m/min using one Fusion H lamp of 300W/inch. Gloss at 60° was measured on cured films using a Multiglossmeter by BYK.

When X is 20%, the gloss at 60 degrees, measured in gloss units, is referred to as the matting efficiency in the rest of the description.

General Description of the Invention

It is a first object of the present invention to provide a matting paste for use as a matting agent in a cationic

system comprising a matting monomer and an amorphous silica in a weight by weight ratio 2-4:1.

Preferably, the amorphous silicas used in this invention has a pore volume between 1.0 and 2.0 ml/g, preferably at least 1.8 ml/g as measured by Nitrogen Porosimetry, a surface area between 200 and 500 sq.m/g and an average particle size, as measured by Malvern between 4.0 and 12.0 microns.

In another preferred embodiment of the invention, the amorphous silica is a wax coated silica which, before coating, has a pore volume between 1.0 and 2.0 ml/g, preferably at least 1.8 ml/g as measured by Nitrogen Porosimetry, a surface area between 200 and 500 sq.m/g and an average particle size, as measured by Malvern between 4.0 and 12.0 microns. In this embodiment, the wax coating preferably represents 6 to 15% by weight of the weight of the uncoated silica. Preferably also, the wax comprises a microcrystalline wax or a polyethylene wax.

Preferably also the matting monomer is selected within the group consisting in vinyl ether monomer containing one or more functional groups and acrylate monomer containing one or more functional groups or mixtures thereof. More preferably the matting monomer is selected within the group consisting in Triethylene glycol divinyl ether (DVE-3), 1,4-Cyclohexane dimethanol divinyl ether (CHVE), Hexanedioldivinylether, Ethylvinylether, Propylvinylether, Isobutylvinylether, Hexanedioldivinylether, Tripropylenglycole triacrylate (TPGDA), Dipropylenglycole diacrylate (DPGDA), 1,6-Hexanediol diacrylate (HDDA), Trimethylpropane triacrylate (TMPTA), Ethoxylated trimethylpropane triacrylate (EO-TMPTA), Propoxylated glycerol triacrylate (GPTA), Triethylenglycol diacrylate, and a mixture thereof.

It is second object of the present invention to provide a photocurable cationic system comprising 40 to 80% w/w of an epoxy resin and 20 to 60% w/w of a matting paste.

Preferably, the epoxy resin is selected within the group consisting in cycloaliphatic epoxy resin or a bisphenol A epoxy resin or a mixture thereof.

It is a third object of the present invention to provide a photocurable cationic system comprising 40 to 80% w/w of an epoxy resin with a matting efficiency of less than 40 gloss units, preferably less than 30 gloss units, more preferably less than 20 gloss units. Preferably, the epoxy resin is selected within the group consisting in cycloaliphatic epoxy resin or a bisphenol A epoxy resin or a mixture thereof.

#### General Description of the Invention

The present invention will be further described in the following examples.

#### Example 1 (Comparative)

Formulations can be manufactured either by successive addition of the various components or by making a matting paste with silica and the matting diluent that can be used to add to the gloss paint for the purpose.

The reference formulation is:

UVR6110*	71.5%	Cycloaliphatic epoxy
Tone Polyol*	10%	Polyol
UVR6990*	3.0%	Cationic photoinitiator
Fluorad FC430#	0.5%	Flow additive
Silica	15%	



\* ex. Union Carbide

# ex. 3M

This produces, with the Silicas at Table 1, in 25  $\mu$ m films on Leneta 7C cards, cured at 3m/min using one Fusion H lamp of 300W/inch, the values of gloss reported.

Silica	Gloss at 60°, in
HP270	72
HP39	88
UV70C *	79
EBN	91
EBC *	87
ED30 *	88
OK412 *	90
No silica	91

\* Wax coated silicas

All the silicas except ED30 (Syloid ED30 from WR Grace) and OK412 (Acematt OK412 from Degussa) are commercially available silicas obtainable from Crosfield under the tradename Gasil.

#### Example 2 (Comparative)

Another reference formulation was used from which, when comparing with example 1, Tone Polyol was removed.

UVR6110	86.5%	Cycloaliphatic epoxy
UVR6990	3.0%	Cationic photoinitiator
Fluorad FC430	0.5%	Flow additive
Silica	10%	

Two silicas were tested and the gloss at 60° was as follows.

Silica	Gloss at 60°
HP270	90
UV70C	85

Example 3 (Invention)

When, in the formulation according to Example 2, part of the UVR6110 is replaced by X parts of CHVE or DVE, the gloss value at Table 2 are obtained for the following formulation.

UVR6110	81.5 - X%
Vinyl ether	X
UVR6990	3.0%
Fluorad FC430	0.5%
Silica	15%

Silica	DVE%	CHVE%	Gloss at 60°
None		40	80
UV70C	12.5		45
UV70C	25		10
UV70C	30		11
UV70C	20		39
HP270	20		24
EBC	20		42
EBN	20		45
HP39	20		37
ED30	20		63
OK412	20		57
UV70C		20	78
UV70C		30	35
UV70C		40	15
HP270		40	13
HP39		40	4

#### Example 4 (Invention)

Similar results are obtained with another class of diluents, namely acrylates. This is the case of so called "hybrid" formulation, containing both a photoinitiator for cationic cure and one for free radical cure which has the following composition.

10

UVR6110 86-X%

UVR6990 3%

Fluorad F-430 0.5%

Acrylated diluent X %

5 Irgacure 184@ 0.5%

Silica 10%

@ex.Ciba Geigy

10 In which the acrylated diluent is any of the following group  
(1,6-hexanediol diacrylate (HDDA), and tripropylenglycole  
triacylate (TPGDA)) and Irgacure 184 is a free radical  
photoinitiator. Results obtained from Formulation 3 are  
reported in Table 3.

15

Silica	%HDDA	%TPGDA	Film thickness in $\mu\text{m}$	Gloss at 60°
UV70C	20		12	52
UV70C	20		25	66
UV70C	40		12	41
UV70C	40		25	47
UV70C		20	12	50
UV70C		20	25	63
UV70C		40	12	42
UV70C		40	25	52

20

25

Claims

1. Matting paste for use as a matting agent in a cationic system comprising a matting monomer and an amorphous silica in a weight by weight ratio 2-4:1.
2. Matting paste according to claim 1 wherein the amorphous silica has a pore volume between 1.0 and 2.0 ml/g, preferably at least 1.8 ml/g, a surface area between 200 and 500 sq.m/g and an average particle size between 4.0 and 12.0 microns.
3. Matting paste according to claim 1 wherein the amorphous silica is a wax coated silica which, before coating, has a pore volume between 1.0 and 2.0 ml/g, preferably at least 1.8 ml/g as measured by Nitrogen Porosimetry, a surface area between 200 and 500 sq.m/g and an average particle size, as measured by Malvern between 4.0 and 12.0 microns.
4. Matting paste according to claim 3 wherein, the wax coating preferably represents 6 to 15% by weight of the weight of the uncoated silica.
5. Matting paste according to claim 2 or 3 wherein the matting monomer is selected within the group consisting in vinyl ether monomer containing one or more functional groups and acrylate monomer containing one or more functional groups or mixtures thereof.
6. Matting paste according to claim 5 wherein the matting monomer is selected within the group consisting in Triethylene glycol divinyl ether (DVE-3), 1,4-Cyclohexane dimethanol divinyl ether (CHVE), Hexanedioldivinylether, Ethylvinylether,

Propylvinylether, Isobutylvinylether,  
Hexanedioldivinylether, Tripropylenglycole triacrylate  
(TPGDA), Dipropylenglycole diacrylate (DPGDA), 1,6-  
Hexanediol diacrylate (HDDA), Trimethylpropane  
5 triacrylate (TMPTA), Ethoxylated trimethylpropane  
triacrylate (EO-TMPTA), Propoxylated glycerol  
triacrylate (GPTA), Triethylenglycol diacrylate, and a  
mixture thereof.

- 10 7. Photocurable cationic system comprising 40 to 80% w/w  
of an epoxy resin and 20 to 60% w/w of a matting paste.
8. Photocurable cationic system comprising 40 to 80% w/w  
15 of an epoxy resin with a matting efficiency of less  
than 40 gloss units, preferably less than 30 gloss  
units, more preferably less than 20 gloss units.
9. Photocurable cationic system according to claim 7 or 8  
20 wherein the epoxy resin is selected within the group  
consisting in cycloaliphatic epoxy resin or a bisphenol  
A epoxy resin or a mixture thereof.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/GB 98/01588

## A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C09D 7/12, C09C 1/30 // C09D 163/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C09C, C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5221337 A (GEORG LUERS ET AL), 22 June 1993 (22.06.93), column 3, line 35 - line 61, claim 1, abstract	1-4
A	WO 9531508 A1 (CROSFIELD LIMITED), 23 November 1995 (23.11.95), claim 1, abstract	1-9
A	US 5460857 A (STEPHAN SCHUNCK), 24 October 1995 (24.10.95), column 1, line 23 - line 32; column 2, line 31 - line 32; column 3, line 43 - line 55, column 5, line 44 - column 6, line 12; abstract	1-9

☐ Further documents are listed in the continuation of Box C.
 ☒ See patent family annex.

\* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document not published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another criterion or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"Z" document member of the same patent family

Date of the actual completion of the international search

18 August 1998

Date of mailing of the international search report

10.09.1998

Name and mailing address of the ISA/


 European Patent Office, P.O. Box 5818 Patentlaan 2  
 NL-2280 HV Rijswijk  
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
 Fax: (+31-70) 340-3016

Authorized officer

BARBRO NILSSON

# INTERNATIONAL SEARCH REPORT

Information on patent family members

27/07/98

International application No.

PCT/GB 98/01588

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5221337 A	22/06/93	AT 119929 T	15/04/95
		AU 638544 B	01/07/93
		AU 7093691 A	15/08/91
		CA 2035675 A	15/08/91
		CS 9100382 A	15/09/91
		DE 4004468 C,R	22/08/91
		DE 69108071 D,T	20/07/95
		EP 0442325 A,B	21/08/91
		FI 910696 A	15/08/91
		DE 4032619 A,C,R	16/04/92
WO 9531508 A1	23/11/95	AT 167507 T	15/07/98
		AU 2308095 A	05/12/95
		DE 69503047 D	00/00/00
		EP 0759959 A,B	05/03/97
		GB 9409388 D	00/00/00
US 5460857 A	24/10/95	AT 118379 T	15/03/95
		BR 9206107 A	10/10/95
		CZ 9302667 A	13/04/94
		DE 4118731 A	10/12/92
		DE 59201420 D	00/00/00
		DK 587591 T	17/07/95
		EP 0587591 A,B	23/03/94
		ES 2071503 T	16/06/95
		HU 67387 A	28/04/95
		HU 9303464 D	00/00/00
		PL 168037 B	30/12/95
		SK 137693 A	11/05/94
		WO 9221450 A	10/12/92